

MOBILE ELEMENT STUDIES IN ROCKS (RAT) FROM COLUMBIA HILLS / WEST SPUR AT GUSEV. M. N. Rao¹, L. E. Nyquist², S. R. Sutton³, and D. H. Garrison¹, ¹ESCG-Jacobs, NASA Johnson Space Center, Houston. TX. 77058; ² ARES, NASA Johnson Space Center, Houston. TX. 77058; ³Department of Geophysical Sciences and CARS, University of Chicago, Chicago. IL. 60637.

Introduction: Using elemental abundances determined by SPIRIT APX spectrometer on rocks and soils at Gusev Plains and Columbia Hills/ West Spur regions, the Athena Team discussed the aqueous geochemical implications at these sites on Mars. They suggested that these rocks were exposed to variable degrees of aqueous alteration (low to high) at Gusev crater [1-3]. Earlier, we developed analytical procedures for studying aqueous geochemical behavior of fluids on rocks at Meridiani [4]. In the present study, we apply these methods to rocks at Columbia Hills/West Spur in order to understand the significance of the Gusev rock results in reference to aqueous geochemical processes on Mars. The data analysis procedure is based on treating SO₃ ("a") and Cl ("b") as two variables and tracking the relationship between "a" and "b" when the fluids undergo evaporation. This process of evaporation leads to concentration changes in these two elements finally producing salt assemblages on Martian rocks. In some cases on plotting "a"/ "b" versus "b" in salt assemblages, they yield a hyperbolic distribution. The relationship is transformed into a straight line when "a"/"b" is again plotted against 1/"b" in the system [5,6]. Earlier, we used this procedure in the case of Meridiani (RAT) rocks [4] and in this study, we discuss the application of this procedure to Gusev rocks.

For understanding the behavior of fluids that interacted with rocks at Gusev, we study the mobile element distribution (S and Cl) in secondary mineral assemblages of rocks (RAT) at Columbia Hills/West Spur (Gusev) using Spirit APXS data [2]. Here, we use RAT data and BRUSH data in appropriate cases as the "AS-IS" data contain some soil contribution. In Fig.1, we plot the RAT rock data from Columbia Hills/West Spur, i.e. Peace (Pe), Fools Gold (FoGo), Pot of Gold (PoGo), Bread Box (B-Box), Alligator (Al), Clovis (Cl), Ebenezer (Eb), Uchben (Uc) and Lutefisk (Lufi). The data points, (though they show large scatter), indicate that the sulfate decreases from ~13% to ~2% as the Cl increases from ~0.5% to ~2.5%.

The scatter of the individual data points representing the rocks may partly be due to the fact that the absolute abundances of SO₃ and Cl are controlled by the modal abundances of mobile element-bearing phases (sulfates/chlorides) and mobile element-poor phases (hematite/silica/clays etc) mixed in varying proportions in the APXS analysis volume of a given rock (phase-mixing). Also, geometry effects may vary from

one rock to another and they may lead to small variations in X-ray signal strength measurements, thereby resulting in variations in absolute abundance estimation. Hence, study of SO₃/ Cl ratios, instead of absolute abundances in these rock samples might overcome, to a large extent, problems related to dilution effects due to "phase-mixing" and the influence of "geometry effects" on x-ray signal strength from one rock to another.

The fluids from which water is gradually removed by evaporation could produce salts: (a) by direct precipitation from evaporatively concentrating solutions when the ion activity product of the salt constituents exceeds their solubility product and/or (b) by dessication of the residual brine pockets left behind on rocks during evaporative concentration of fluids in the system. The concerned mineral phases are assumed not precipitate before the steady state condition is reached. When sulfate-rich solutions undergo evaporative concentration, salts crystallizing from early stages of brine evolution might yield high SO₃ and low Cl [7-9].

Considering that SO₃ and Cl behave as conservative elements in acidic solutions, we plot the Cl abundance on the ordinate and the SO₃/Cl ratio on the abscissa in Fig.2 for the Columbia Hills/West Spur rocks (RAT). The data points (showing much less scatter) seem to fit to a possible hyperbolic distribution. The data points can be fitted to an equation of the type (SO₃/Cl)_m = a / (Cl)_m + b, which defines a hyperbola when the x-variable is (Cl)_m. The numerical values of a and b define the position and curvature of the hyperbola [5,6]. If the hyperbolic relation is valid, this relation is transformable into a straight line by plotting the X-coordinate as the inverse of Cl abundance, i.e. 1/(Cl)_m. This procedure leads to the following relation (SO₃/Cl)_m = aX + b where X = 1/(Cl)_m. This equation corresponds to a straight line with slope a and intercept b on the Y-axis [5,6]. The underlying assumption in this procedure is that the participating species (SO₃ and Cl) behave conservatively in the acidic solutions and the compositions of the resulting sulfate/chloride salt assemblages are not altered by other processes after deposition.

Accordingly the SO₃/ Cl ratios for Columbia Hills/West Spur rocks (RAT) and outcrops are plotted against 1/ Cl in Fig.3. The goodness of the fit for the plotted data points in Fig. 3 provides a test for the validity of the above assumptions. The data fit (correlation coefficient r² = 0.8) justifies the assumption that

the mobile elements S (as sulfate) and chloride behave conservatively in the evaporating solutions at the Columbia Hills site at Gusev. Such relationship between sulfate and chloride could be maintained if the aqueous solutions are acidic in nature.

The salt assemblages on rocks from Gusev Plains show a different kind of behavior between sulfate and chloride when compared to that in Columbia Hills / West Spur. The data points shown in the oval field in Fig. 3 represent the Gusev Plains (RAT) rocks (Adirondack, Humphry, Mazatzal, Wishstone, Champagne, Watchtower, and Wooly Patch). These data points do not show any correlation between SO_3/Cl and $1/\text{Cl}$ suggesting that the nature and composition of salts deposited on these rocks is different from that of the Columbia Hills / West Spur rocks (RAT). Furthermore, the SO_3/Cl ratio in all the the “Plains” rocks seems to be similar (within a factor of 2) suggesting that they were probably exposed to one kind of infiltrating fluid at Gusev for a short period of time. One possible explanation is that the infiltrating solutions interacted with the Gusev Plains rocks for a short time and the solutions moved away quickly (e.g. flow) from the sites where the rocks are situated at Gusev.

In this context, based on topographic considerations, [10] suggested that the landing area (C3 crater) of Spirit is located in one of the deepest lows at Gusev and thus would have attracted subsurface flow and promoted near surface ponding of water on Mars.

This study shows that the Gusev Plains rocks were exposed to low SO_3/Cl solutions (sulfate-poor) for short period of time (weak interaction), whereas solutions with high SO_3/Cl ratios (sulfate-rich) seem to have pervasively interacted with Columbia Hills/ West Spur rocks (strong interaction) at Gusev crater. Our conclusions seem to be consistent with the Mossbauer results given for these rocks by [11].

References: [1] Arvidson R. V. et al. (2006) *JGR*, 111, E02S01, doi: 10.1029/ 2005JE002499. [2] Gellert R. et al. (2006) *JGR*, 111, E02S05, doi: 10.1029/2005JE002555. [3] Ming D. W. et al. (2006) *JGR*, 111, E02S12, doi: 1.1029/ 2005JE002560. [4] Rao M. N. et al. (2006) International Mars Conf. 7th, JPL. #3174.. [5] Faure G. (1998) *Principles and Applications of Geochemistry*, Prentice-Hall, Upper Saddle River, N.J. [6] Langmuir C. H. et al. (1978) *EPSL*, 37, 380-392 [7] Hardie L. A. and Eugster H. P. (1970) *Mineral. Soc. Am. Spec. paper*, 3, 273-290. [8] Sanford W. E. and Wood W. W. (1991) *Am. J. Sci.* 291, 687-710. [9] Ingebritsen S. E. and Sanford W. E. (1998) *Evaporites: In Ground Waters in Geological Processes*, Cambridge University Press, New York. [10] Cabrol N. A. et al. (2006) *JGR*, 111, E02S20, doi:

10.1029/2005JE002490. [11] Morris R. V. et al. (2006) *JGR*, 111, doi: 10.1029/2005JE002584.

Figure Captions: Fig.1. $[\text{Cl}]$ vs $[\text{SO}_3]$ for Columbia Hills/ West Spur RAT rocks. names of the rocks corresponding to the abbreviations are given in the text. Note the large scatter. Fig. 2. SO_3/Cl vs Cl for the same rocks at Columbia Hills/West Spur (much less scatter). Fig. 3. SO_3/Cl vs $1/\text{Cl}$ plot for Columbia Hills/West Spur and Gusev Plains rocks.

